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PATENT SPECIFICATION

(11) 1 517 362

(21) Application No. 34617/75 (22) Filed 20 Aug. 1975

(44) Complete Specification published 12 July 1978

(51) INT CL² B01D 13/00 B63C 11/24

(52) Index at acceptance

B1L 103 201 203 215 217 309 319 AE

A5T 311 464

C1A S171 S181 S18Y S475 S492 S60Y S61X S711 SB

(19)

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(54) SEPARATIVE BARRIER FOR PREFERENTIAL TRANSPORT OF CO_2 AND APPARATUS EMPLOYING SAME

(71) We, HYDRO-MEMBRONICS, INC., a corporation organised under the laws of the State of New York, United States of America, of 331 Southwood Circle, Syosset, New York 11791, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the separation under water of CO_2 from a mixture of CO_2 and other gases. More particularly, it relates to apparatus for accomplishing such separation at a relatively rapid rate with high efficiency.

While not limited thereto, the present invention is especially suited to removing CO_2 from a life support system, and particularly from underwater breathing apparatus of the rebreather type. As is well known, basic underwater breathing apparatus (usually referred to as scuba equipment) consists of one or more pressurized air tanks equipped with a demand valve and a breathing mask or mouthpiece including an arrangement of check valves whereby air is inhaled from the tanks and exhaled directly into the water. Since the human body utilizes only a minor proportion of the air inspired with the major proportion being exhaled to purge the lungs of CO_2, the conventional apparatus is very wasteful. Typically, a diver using such conventional basic apparatus is limited to about 20 minutes under water at a depth of 100 feet.

To extend diving time, there has been experimentation with closed circuit rebreather systems relying on the use of chemicals to absorb CO_2 from expired air. Calcium oxide has been used for this purpose but not without considerable risk since calcium oxide converts to a caustic in the presence of moisture and it is limited as to the quantity of CO_2 that it can absorb.

It has been known for a long time that a silicone rubber membrane, through the phenomenon known as selective solubility diffusion, will separate CO_2 from the other components found in air. An above water filter constructed from silicone rubber is described in United States patent No. 3,369,343. It is also suggested in said patent that the silicone rubber membrane can be used to extract oxygen and nitrogen from water to support life and such a system is described in United States patent No. 3,318,306. Another system which involves the removal of CO_2 from exhaled air and its replacement by oxygen extracted from water through a selective diffusion permeable membrane such as a silicone rubber wall is described in United Kingdom patent specification No. 1,037,090.

A closed rebreather-respirator circuit is described in United States patent No. 3,489,144, wherein a silicone rubber membrane is used in a rebreather unit for purging CO_2 and water vapor from exhaled gases. The rebreather unit recycles air for rebreathing from which CO_2 has been purged and which has been augmented with oxygen from a supply tank. Purging air is circulated through the rebreather unit to carry off CO_2.

However, none of the known systems has proven satisfactory for use in self-contained underwater breathing apparatus to extend the dive time for an individual. One major drawback is the relatively low permeability of silicone rubber for CO_2 even though it is about five times greater than that for oxygen. Hence, the size of a unit for providing effective removal of CO_2 is prohibitive.

Wholly unrelated to the field of life support equipment, research has been conducted on the effect of catalysts on the reaction between CO_2 and water. An article, entitled "The Catalysis of the Reaction Between Carbon Dioxide and Water", published in the Journal of the Chemical Society (A), 1966, 812, includes at page 814 the following table of anions having catalytic activity in the foregoing reaction:

$[B(OH)_4]^-$, $H_3SiO_4^-$, $H_3GeO_4^-$, HPO_4^{--}, $H_2PO_4^-$, $HAsO_4^{--}$, AsO_2^-, SO_3^{--}, $TeO(OH)_5^-$, $Te(OH)_4O_2^{--}$, $HTeO_3^-$, ClO^-, BrO^-, SeO_3^{--}, and Phenolate.

In United States patent No. 3,396,510, there is described the enhancement of the reaction of CO_2 with water by the addition of certain named catalysts. All of the anions of said catalysts are included in the foregoing table set forth in the above-mentioned article. Said last mentioned patent also describes the use of an immobilized liquid film as the permeable membrane with one of said catalysts being included in said liquid.

With the foregoing as background, it is an object of the present invention to provide an improved separative barrier for the preferential separation under water of CO_2 from a mixture of CO_2 and other gases.

It is a further object of the present invention to provide underwater breathing apparatus affording a very substantial increase in dive time over conventional scuba equipment.

In accordance with one aspect of the present invention, there is provided a separative barrier for the preferential transport of CO_2 from a mixture of CO_2 and other gases to water which comprises a porous membranous element impregnated with a catalyst for hydration of CO_2 and having hydrophobic pores, said element being exposed on opposite sides for direct contact with said water and said mixture respectively.

In accordance with a further aspect of the present invention, there is provided underwater breathing apparatus comprising in combination means for storing under pressure a life supporting gaseous medium, means comprising a container having an inlet and an outlet and walls for excluding water from its interior, said walls comprising a separative barrier as defined above, a pressure regulated outlet coupled to said storing means, respiratory tract coupling means, means coupling both said pressure regulated output and said container outlet to said respiratory tract coupling means for supplying life supporting gas thereto on demand, means for feeding expiration from said respiratory tract coupling means to said container inlet, and means for conducting said expiration through said container from said container inlet to said container outlet in contact with said separative barrier.

A detailed description of the presently preferred embodiments of the invention will now be described with reference to the appended drawings in which:

Figure 1 is a rear view of a diver equipped with underwater breathing apparatus constructed in accordance with the subject invention;

Figure 2 is a side view of the diver of Figure 1;

Figure 3 is a plan view partially schematic illustrating the breathing apparatus employed by the diver in Figures 1 and 2;

Figure 4 is a diagrammatic sectional view through a separative barrier as employed in the breathing apparatus of Figure 3; and

Figure 5 is a view similar to Figure 4 showing a modification thereof.

The same reference numerals are used throughout the various figures of the drawings to designate the same or similar parts.

Referring now to Figures 1, 2 and 3, there is shown a typical diver 10 equipped for underwater activity with underwater breathing apparatus 11. The apparatus 11 includes a pressure tank 12 for storing under pressure a life supporting gaseous medium. In the present example, such medium is preferably a mixture of seven parts oxygen and one part nitrogen. A container 13 having an inlet 14 and an outlet 15 has said outlet 15 connected by tubing 16 to a mouthpiece 17 for coupling in the usual manner with the respiratory tract of the diver. A check valve 18 is provided between the mouthpiece 17 and tubing 16, as shown. Another section of tubing 19 interconnects the inlet 14 of the container 13 with the mouthpiece 17 and includes a check valve 20, as shown. A demand valve 21 is interposed between the tank 12 and the tubing 16.

The container 13 has a substantial portion of its exposed walls formed from a separative barrier which comprises a porous hydrophobic membranous element. The interior of the container 13 may be provided with baffles shown diagrammatically at 22 for causing the gas flowing through the container between the inlet 14 and the outlet 15 to follow a serpentine or labyrinthian path. The interior may be constructed in any well-known manner for causing the gas as it passes through the container to come in contact with the aforementioned separative barrier material which will now be described.

Referring to Figure 4, there is shown in detail the separative barrier wall from which the container 13 may be constructed. The base element is in the form of a woven polyester mono-filament fabric 23 which has been impregnated with a non-wetting agent selected from the group consisting of silicone and fluorocarbon resins. Said non-wetting agent is shown diagrammatically in Figure 4 by the layer 24. It should be understood that said non-wetting agent penetrates the pores of said fabric 23 without sealing such pores. The coated fabric is thus both hydrophobic and porous. This, in turn, is impregnated with an hydration catalyst for hydration of CO_2. The catalyst is shown schematically by the layer 25.

In one presently preferred construction of the barrier or membrane illustrated in Figure 4, use was made of a fabric of polyester mono-filament having a thread count of approximately 41×34, a thickness of about 12-1/2 mil, and a weight of approximately 2-1/2 ounces per sq. yd. Such fabric was purchased from Stern & Stern Textiles, Inc.,

of Hornell, New York, under their style number 15622. Said fabric was spray coated with a polytetrafluoroethylene coating obtained from Bel-Art Products of Pequannock, New Jersey, and identified by that company as solution No. F24012 which said company markets under their trademark "Fluo-Kem". Said coated fabric was then impregnated with calcium hypochlorate. Through laboratory experiments it has been clearly established that a submerged container provided with a wall of porous hydrophobic membranous material produced as described above contains oxygen for an indefinite period while releasing CO_2 at a rapid rate.

As shown in Figure 4, CO_2 is actively transported from expired air through the wall of the separative barrier to the surrounding water. The chemical reaction involves the combination of CO_2 with the water to produce carbonic acid which then dissociates to yield bicarbonate and hydrogen ions. As explained in the above-mentioned article on the catalysis of said reaction, any material may be used as a catalyst which contains anions selected from at least one member of the group consisting of those set forth in the aforementioned table.

Other porous hydrophobic membranous elements may be employed in addition to the type described with reference to Figure 4. For example, as shown in Figure 5, instead of the woven fabric, use may be made of a layer of porous polymer 26 where the polymer is selected from the group consisting of polytetrafluoroethylene and polypropylene. The surface of the porous polymer is then impregnated with an hydration catalyst selected from the above mentioned group of catalysts. This is shown diagrammatically by the layer 27. As also shown in Figure 5, the pores such as 28 pass through the layer 27 such that CO_2 can pass through said pores and reach the interface with the surrounding water.

Referring again to Figure 3, it should be understood that when the diver inhales, via mouthpiece 17, air or a breathing mixture will be drawn both from the tank 12 and from the container 13 via the check valve 18. When the diver exhales the expired air or gaseous mixture will pass through the check valve 20 and through the tubing 19 and inlet 14 into the container 13. Thereupon the gaseous mixture will be exposed to the porous hydrophobic membranous walls of the container 13 for extraction of the CO_2.

To summarize, the porous structure should be constructed from a base element having the necessary tensile strength for withstanding the pressures in use. Suitable structural support members, not shown in the accompanying drawings, may be incorporated in any known manner. The base member must be hydrophobic in nature either by virtue of its own characteristics or because of a surface treatment. Finally, a suitable catalyst is included for enhancing the reaction of CO_2 with water. Although not previously mentioned, carbonic anhydrase is also useful as a catalyst. The pores themselves must be hydrophobic (in general therefore less than 50 microns in size) and of a size and shape which affords freedom from clogging.

Experimentation has revealed that a membrane constructed in accordance with the present invention will transport CO_2 at a rate of 1240 ml/min/m^2/atm. To afford a further indication of the efficacy of the subject invention, it is estimated that a working diver having a weight of 160 lbs. and consuming oxygen at the rate of 750 ml/min with an alveolar ventilation of 18 l/min could remain submerged at a depth of 100 feet employing the subject rebreather system along with a tank capacity of 72 cu. ft. holding an oxygen-nitrogen mixture in the ratio of 7 to 1 for a period of approximately 20 hours. By way of contrast, the same diver using a tank filled with ordinary air and without the rebreather system of the present invention could remain submerged at a depth of 100 feet for only approximately 30 minutes.

WHAT WE CLAIM IS:—

1. A separative barrier for the preferential transport of CO_2 from a mixture of CO_2 and other gases to water, comprising a porous membranous element impregnated with a catalyst for hydration of CO_2 and having hydrophobic pores, said element being exposed on opposite sides for direct contact with said water and said mixture respectively.

2. A separative barrier according to Claim 1, wherein said membranous element consists essentially of a woven polyester monofilament fabric impregnated with a non-wetting agent selected from the group consisting of silicone and fluorocarbon resins.

3. A separative barrier according to Claim 1, wherein said membranous element consists essentially of a layer of porous polymer where the polymer is selected from the group consisting of polytetrafluoroethylene and polypropylene.

4. A separative barrier according to any one of the preceding claims wherein said catalyst contains at least one anion selected from the group consisting of

$[B(OH)_4]^-$, $H_3SiO_4^-$, H_3GeO_4, HPO_4^-, $H_2PO_4^-$, $HAsO_4^{--}$, AsO_2^-, SO_3^{--}, $TeO(OH)_5^-$, $Te(OH)_4O_2^{--}$, $HTeO_3^-$, ClO^-, BrO^-, SeO_3^{--}, and Phenolate.

5. Underwater breathing apparatus comprising in combination means for storing under pressure a life supporting gaseous medium, means comprising a container having an inlet and an outlet and walls for

excluding water from its interior, said walls comprising a separative barrier according to any one of the preceding claims, a pressure regulated outlet coupled to said storing means, respiratory tract coupling means, means coupling both said pressure regulated outlet and said container outlet to said respiratory tract coupling means for supplying life supporting gas thereto on demand, means for feeding expiration from said respiratory tract coupling means to said container inlet and means for conducting said expiration through said container from said container inlet to said container outlet in contact with said separative barrier.

6. Apparatus for use in underwater breathing apparatus for eliminating CO_2 from expiration comprising a container having an inlet and an outlet and walls for excluding water from its interior, said walls comprising a separative barrier according to any one of Claims 1 to 4 and means for conducting expiration through said container from said inlet to said outlet in contact with said separative barrier.

7. A separative barrier substantially as shown in Figures 1 to 4 or Figures 1, 2, 3 and 5 of the accompanying drawings and described herein with reference thereto.

8. Underwater breathing apparatus substantially as described with reference to the accompanying drawings.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1517362 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale

Fig.1.

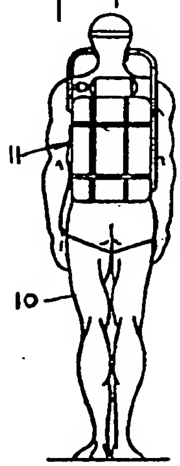

Fig.2.

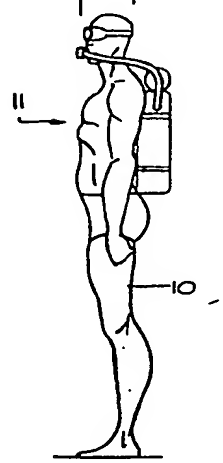

Fig.3.

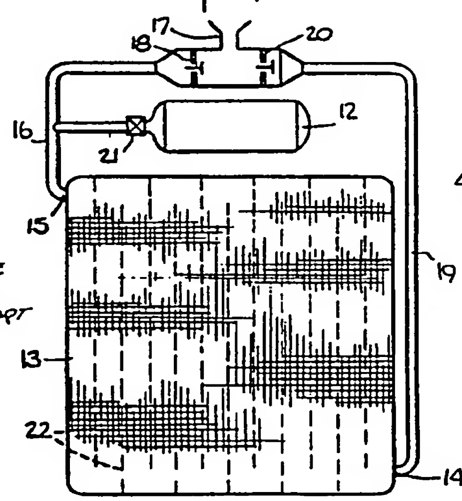

Fig.4.

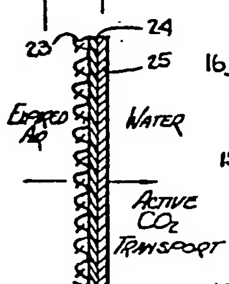

Fig.5.